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File: USPT

Aug 7, 1984

DOCUMENT-IDENTIFIER: US 4464281 A

TITLE: Stabilized bleach-sensitive dyes in automatic dishwasher detergent compositions

Abstract Paragraph Left (1):

A method for stabilizing automatic dishwasher detergents containing bleach-sensitive dyes against decolorization by the bleaching agents of the compositions. The detergent powders comprise about 5-70% of a builder, 1-15% of a nonionic surfactant, 1-20% of a silicate, 0-60% of a filler, 0.001-0.1% of a bleach-sensitive dye, water and a bleaching agent. Prior to the addition of bleaching agent, the composition is pre-conditioned by contact with a flow of air. The resultant powder has a color that remains essentially unchanged even after storage for two months at elevated temperatures.

Brief Summary Paragraph Right (39):

Other N-bromo and N-chloro imides may also be used such as N-brominated and N-chlorinated succinimide, malonimide, phthalimide and naphthalimide. Other compounds include the hydantoins, such as 1, 3-dibromo and 1,3-dichloro-5,5-dimethylhydantoin, N-monochloro-C,C-dimethylhydantoin methylene-bis(N-bromo-C,C-dimethylhydantoin); 1,3-dibromo and 1,3-dichloro 5-isobutylhydantoin; 1,3-bromo and 1,3-dichloro 5-methyl-5-ethylhydantoin; 1,3-dibromo and 1,3-dichloro 5,5-isobutylhydantoin; 1,3-dibromo and 1,3-dichloro 5-methyl-5-n-amylhydantoin, and the like. Further useful hypohalite liberating agents comprise tribromomelamine and trichloromelamine.

Brief Summary Paragraph Right (44):

Among the suitable peroxygen active bleaches are potassium, sodium and ammonium salts of persulfate, dipersulfate, peroxide and perborate. Organic peroxides such as lauroyl peroxide are also suitable.

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US006310220	28	1 - 28
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L4: Entry 14 of 108

File: USPT

Oct 10, 2000

DOCUMENT-IDENTIFIER: US 6130198 A

TITLE: Bleaching efficiency boosters for bleach and textile detergent compositions

Brief Summary Paragraph Right (5):

JP-A-07197097 describes bleach compositions which contain a peroxide of the oxygen type, a bleach activator based on acyloxylanilide derivatives and one or more amines, amine salts or quaternary ammonium salts in an amount of at least 1% by weight. In this case, the amines can be the hydrophilic secondary amines diethanolamine, ethanolmethylaniline, diisopropanolamine or N-methylaniline. The compositions are used for bleaching dyed textiles, the intention being to avoid loss of color from the dyeing.

Brief Summary Paragraph Right (6):

JP 06248295 describes bleach compositions which have a long shelf life and high bleaching efficiency and avoid loss of color from textiles. The compositions contain peroxides and a salt consisting of a bleach activator and an aromatic peracid precursor anion and a quaternary ammonium ion in an amount of at least 0.7% by weight, which can be derived from the hydrophilic secondary amines diethanolamine, diisopropanolamine and dimethylamine.

Brief Summary Paragraph Right (12):

EP-A3-0 349 153 describes aromatic secondary amines as radical scavengers for free radicals in liquid hydrogen peroxide compositions which contain no activator.

Brief Summary Paragraph Right (24):

The bleaching efficiency-boosting effect with the claimed amines makes it possible to use the bleach or textile detergent compositions at low temperatures, in particular in the range up to a maximum of 40.degree. C., at which bleach compositions often show inadequate effectiveness. The bleaching efficiency-boosting effect of the amines according to the invention may moreover be further increased by adding suitable bleach activators, with or without additional bleach-stabilizing additives.

Detailed Description Paragraph Right (70):

compositions which, for example, can be employed in detergents and cleaners additionally contain one or more bleach stabilizers. These comprise additives able to adsorb, bind or complex traces of heavy metals. Examples of additives which can be used according to the invention with a bleach-stabilizing action are polyanionic compounds, such as polyphosphates, polycarboxylates, polyhydroxypolycarboxylates, soluble silicates as completely or partially neutralized alkali metal or alkaline earth metal salts, in particular as neutral Na or Mg salts, which are relatively weak bleach stabilizers. Examples of strong bleach stabilizers which can be used according to the invention are complexing agents such as ethylenediaminetetraacetate (EDTA), nitrilotriacetic acid (NTA), methyl-glycinediacetic acid (MGDA), .beta.-alaninediacetic acid (ADA), ethylenediamine-N,N'-disuccinate (EDDS) and phosphonates such as ethylenediaminetetramethylenephosphonate, diethylenetriaminepentamethylenephosphonate or hydroxyethylidene-1,1-diphosphonic acid in the form of the acids or as partially or completely neutralized alkali metal salts. The complexing agents are preferably employed in the form of their Na salts.

Detailed Description Paragraph Right (73):

The main ingredients of textile detergents, bleaches and cleaners are, besides the bleach composition which consists of bleach and, in particular, secondary, amine according to the invention, with or without bleach activator, builders, that is to say inorganic builders and/or organic cobuilders, and surfactants, in particular anionic and/or nonionic surfactants. Besides these, it is also possible for other conventional auxiliaries and additives such as fillers, complexing agents, phosphonates, dyes, corrosion inhibitors, antiredeposition agents and/or soil release polymers, color

transfer inhibitors, bleach catalysts, peroxide stabilizers, electrolytes, optical brighteners, enzymes, perfume oils, foam regulators and activating substances to be present in these compositions if this is expedient.

Detailed Description Paragraph Right (128):

Besides combined detergents and bleaches, suitable formulations of the described bleach compositions for textile laundering are also compositions which are used as additives to peroxide-containing or peroxide-free detergents. They essentially contain the bleach composition consisting of bleach and secondary amine, with or without bleach activator, and, where appropriate, other auxiliaries and additives, especially stabilizers, pH regulators, thickeners and surfactants.

Detailed Description Paragraph Type 1 (7):

N,N-diacylated and N,N,N',N'-tetraacylated amines, such as N,N,N',N'-tetraacetylmethylenediamine and -ethylenediamine (TAED), N,N-diacetylaniline, N,N-diacetyl-p-toluidine or 1,3-diacylated hydantoins such as 1,3-diacetyl-5,5-dimethylhydantoin;

Detailed Description Paragraph Type 1 (50):

0-5% by weight, preferably 0.1-3% by weight, of peroxide stabilizers,

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File: USPT

Sep 5, 1978

DOCUMENT-IDENTIFIER: US 4111826 A
TITLE: Bleaching assistants

Abstract Paragraph Type 1 (2):

(b) 2-25% by weight of a stabilizing agent for percompounds e.g. organic phosphonic acids or ethylenediaminetetraacetate;

Brief Summary Paragraph Right (2):

Detergent compositions which contain so-called bleaching activators in addition to the usual detergent substances having a cleaning action, builders and bleaching percompounds, are known. These activators comprise carboxylic acid derivatives which react with the percompounds, e.g. sodium perborate, with the formation of peracids and therefore increase the bleaching action of the compositions or make it possible to effect bleaching at relatively low or moderate washing temperatures. It is also known to incorporate agents which stabilise percompounds in solutions in detergent bleach compositions. The term "percompounds" is used here to indicate those percompounds which liberate oxygen from their solutions, such as perborates, percarbonates, perphosphates, and persulfates. The stabilising agents known in the art comprise ethylenediaminetetraacetic acid and its alkali metal salts, and the organic phosphonic acids, such as ethane-1-hydroxy-1,1'-diphosphonic acid, amino-trimethylene phosphonic acid and ethylenediaminetetra-(methylene phosphonic acid). In preparing detergent powder compositions by the spray-drying technique these stabilising agents are normally incorporated in the alkaline detergent slurry without difficulty. These stabilising agents, though being present in relatively small proportions, are an important ingredient in such washing compositions, since apart from reducing chemical damage to textiles, they inhibit the deleterious side reaction which occurs in the wash solution between the peracid formed and the percompound to form non-bleaching products, which would result in a loss of bleaching efficiency.

Brief Summary Paragraph Right (3):

Whilst on the one hand the storage properties of washing compositions comprising a bleaching activator and a bleaching percompound can be improved by providing the powder particles of the bleaching activator with an inert protective coating or by forming activator-containing particles from e.g. spray-cooling a molten mixture of the activator and a suitable carrier material, and on the other hand the slurry incorporation of stabilising agents for percompounds does not cause difficulties in preparing a percompound containing detergent bleach composition without an activator, the preparation and storage of washing compositions comprising a bleaching activator, a bleaching percompound and a percompound stabilising agent still pose considerable problems. It has been established that when the stabilising agent is incorporated in the alkaline detergent slurry before spray-drying, it loses its activity quite rapidly in a detergent bleach powder composition comprising an organic bleaching activator.

Brief Summary Paragraph Right (4):

Apparently the stabilising agent not inactivated in the alkaline solution and during spray-drying is converted into a form which is quite sensitive to oxidation by the percompound or percompound/activator combination present in the formulation. Whilst simple post-dosing of the powdered stabilising agent to the spray-dried powder may mitigate said problem to only a certain extent, said measure will also give some practical problems, since relatively small proportions of stabilising agent as required in the washing composition give handling and dosing difficulties, requiring quite accurate dosing equipments. Besides, differences in powder dimensions and bulk density will give rise to undesirable segregation in the pack.

Brief Summary Paragraph Right (6):

The present invention therefore allows bleaching activators and bleaching percompounds to be used in conjunction with stabilising agents in detergent bleach compositions with

greater efficiency than in manners hitherto known.

Brief Summary Paragraph Right (7):

According to the invention, bleaching assistants are provided which can be used for post addition to particulate detergent and bleaching compositions or for addition to washing solutions comprising a peroxide bleach detergent composition.

Brief Summary Paragraph Right (16):

It has been found that in particles as formulated above both the bleaching activator and the stabilising agent retain their activity during storage to a satisfactory extent. When the particles are mixed with percompound bleaching agents and particulate washing compositions they give sufficient protection against undesirable interaction between reactive and sensitive components.

Brief Summary Paragraph Right (17):

The bleaching assistants according to the invention are preferably present in admixture with further particulate bleaching agent components, particularly inorganic percompounds, such as sodium perborate, sodium percarbonate and sodium perpyrophosphate, which in aqueous solution liberate hydrogen peroxide. In such mixtures a suitable proportion by weight of the bleaching assistant to the percompound will be from 3:1 to 1:7.

Brief Summary Paragraph Right (20):

(a) N-diacylated and N,N'-tetraacylated amines, such as N,N,N',N'-tetraacetylmethylenediamine and -ethylenediamine, N,N-diacetylaniline and N,N-diacetyl-p-toluidine, and 1,3-diacylated hydantoins such as, for example, 1,3-diacetyl-5,5-dimethylhydantoin and 1,3-dipropionylhydantoin;

Brief Summary Paragraph Right (34):

Suitable stabilising agents for use in the invention include ethane-1-hydroxy-1,1-diphosphonic acid -- (EHDP); amino-N-alkylidene phosphonic acids, for example aminotri-(methylene phosphonic acid) -- (ATMP), and ethylenediamine tetra-(methylene phosphonic acid) -- (EDTMP), and ethylenediaminetetraacetic acid -- (EDTA) or its alkali metal salts.

Brief Summary Paragraph Right (35):

A preferred stabilising agent according to the invention is ethylenediaminetetra-(methylene phosphonic acid).

Brief Summary Paragraph Right (37):

The bleaching assistant particles of the invention may be obtained by spraying a molten nonionic surface-active compound on to a moving bed of a mechanical mixture of the bleaching activator and the stabilising agent in the appropriate ratio. The temperature of the molten nonionic before spraying should preferably be kept at least 10.degree. C. above the melting point.

Brief Summary Paragraph Right (38):

A suitable equipment for use in the process for preparing the bleaching assistants according to the invention is a continuously operating pan granulator in which the powdered mixture of bleaching activator and stabilising agent is charged on to a slanting rotating plate or pan to form a moving bed, on to which the liquefied nonionic compound is sprayed. Finished granulated particles are discharged at the lower side of the slanting plate after passing a weir.

Brief Summary Paragraph Type 1 (2):

(b) 2-25%, preferably 5-20%, by weight of at least one stabilising agent for percompounds;

Detailed Description Paragraph Right (7):

The following example describes the storage behaviour of ethylenediaminetetraacetate (EDTA), a stabilising agent customarily included in spray-dried perborated powders, and of ethylenediaminetetra-(methylenephosphonic acid) -- (EDTMP) incorporated either in the bleaching assistant or in the spray-dried slurry.

Detailed Description Paragraph Left (1):

The residual activities of stabilising agents after storage for 1, 2, 3 and 4 weeks under various climatic conditions are given below:

CLAIMS:

1. A bleaching assistant in the form of co-granulated particles having a diameter of from 0.2 mm to 3.0 mm for use in or with washing and bleaching compositions, consisting essentially of:

(a) 50 to 85% by weight of at least one bleaching activator for percompounds, having a titre in a peracid formation test of at least 1.5 ml 0.1N sodium thiosulphate, selected from the group consisting of:

- (i) N-diacylated and N,N'-tetraacylated amines;
- (ii) N-alkyl-N-sulphonyl carbonamides;
- (iii) N-acylated cyclic hydrazides;
- (iv) O,N,N-trisubstituted hydroxylamines;
- (v) N,N'-diacyl-sulphurylamides;
- (vi) Triacyl cyanurates;
- (vii) Carboxylic acid anhydrides;
- (viii) Sugar esters;
- (ix) 1,3-Diacyl-4,5-diacyloxy-imidazolidine;
- (x) Tetraacetyl glycoluril and tetrapropionylglycoluril;
- (xi) Diacylated 2,5-diketopiperazines;
- (xii) Acylation products of propylene diurea; and
- (xiii) Carbonic acid esters;

(b) 2 to 25% by weight of at least one stabilizing agent for percompounds selected from the group consisting of:

- (i) ethane-1-hydroxy-1,1-diphosphonic acid, and its alkalimetal salts;
- (ii) aminotri-(methylene phosphonic acid) and its alkalimetal salts;
- (iii) ethylene diamine-tetra-(methylene phosphonic acid) or its alkalimetal salts; and
- (iv) ethylene diamine-tetraacetic acid or its alkalimetal salts; and

(c) 7 to 30% by weight of a nonionic surface-active compound selected from the group consisting of water-soluble polyalkylene oxide adducts of natural or synthetic, primary or secondary alcohols; polyalkylene oxide adducts of fatty acids, polyalkylene oxide adducts of fatty amides; polyalkylene oxide adducts of alkylphenols, each having 5-25 ethylene oxide groups in the molecule and 8-22 carbon atoms in the hydrophobic moiety; and polyethylene oxide adducts of polypropylene glycol containing 20 to 300 ethylene glycol ether groups and 10 to 100 propyleneglycolether groups; said nonionic compound having a melting point of at least 35.degree. C.

2. Bleaching assistant according to claim 1, wherein the stabilising agent is ethylenediaminetetra-(methylenephosphonic acid).